

## NONSTOICHIOMETRIC REACTIONS PRODUCING CERAMIC PIGMENTS

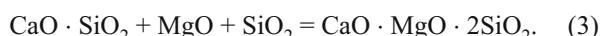
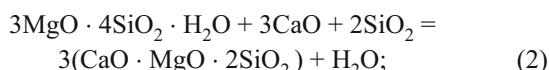
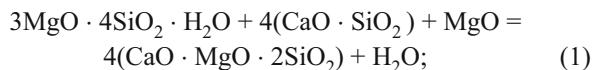
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The reactions synthesizing diopside ceramic pigments using natural minerals — talc and wollastonite — have been investigated. For the initial components taken in a nonstoichiometric ratio the yield of the main reaction product — diopside — increases in two of the three reactions studied, while in the third reaction a change of the stoichiometry of the input components results in a lower content of diopside. It is found that for a small deviation from stoichiometry the dominant crystal structure of the pigment changes, which in turn fundamentally changes the color of the pigment.

**Key words:** talc, wollastonite, diopside, synthesis, chromophore, ceramic pigments.

There are many advantages to synthesizing ceramic pigments using natural mineral raw materials: the calcination temperature of the pigments decreases and raw-materials costs decrease. Using the structures of natural raw materials as the base structures, ceramic pigments with derivative crystal structures can be developed by mixing in pure oxides or other minerals. For example, the natural minerals talc and wollastonite make it possible to obtain ceramic pigments with diopside structure [1, 2]:



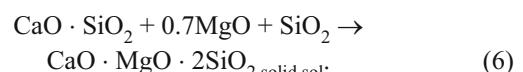
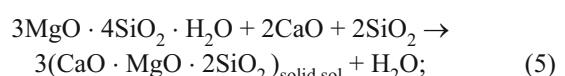
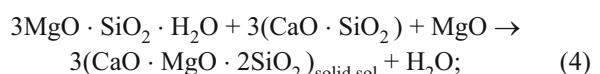
However, the nonuniform multiphase composition of the products is a problem for synthesis. Wollastonite, magnesium metasilicate, and forsterite are identified in addition to diopside.

It is known that during the synthesis of complex oxides from simple oxides the difference in the coefficients of diffusion of the cations present in them can result in a deviation from stoichiometry. A solid solution of one of the oxides in the stoichiometric compound and phase, consisting of a second oxide or enriched by it, is formed from a mixture of simple oxides with a stoichiometric composition. A uniphase material can be obtained by taking an oxide with the higher

diffusion coefficient of the cation in a deficient amount as compared with the stoichiometric ratio [3].

In the present work, to increase the yield of the main reaction product, decreasing the amount of the phases contained in the reaction products, and improving the uniformity of the pigment composition the reactions presented were studied with a nonstoichiometric ratio of the initial components.

In the first reaction the amount of wollastonite was decreased, and in the second and third reactions the content of the oxides CaO and MgO was decreased; the cations of the latter oxides have higher diffusion coefficients as compared with silicon oxide and elements of the structure of the natural minerals [4]. The adjusted reactions are as follows:



The nonstoichiometric compositions obtained fall into the crystallization field of diopside: the compositions with respect to the reactions (4) and (5) fall into the region of formation of magnesium metasilicate, the compositions according to the reaction (6) border on the region of formation of the solid solutions with wollastonite.

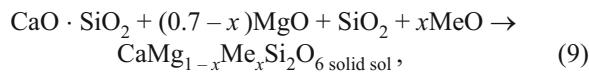
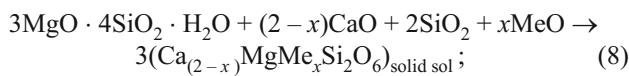
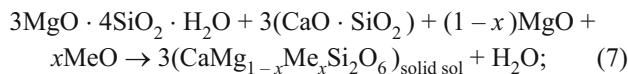
In the present work, low-iron talc from the Algui deposit and enriched micaceous wollastonite in which the content of

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the main mineral was 98 and 85%, respectively, were used. The chemical composition is presented in Table 1.

Chromophores — compounds of *d* elements —  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  — were introduced in the form of salts in the amounts 0.1 – 1 moles in terms of oxide:



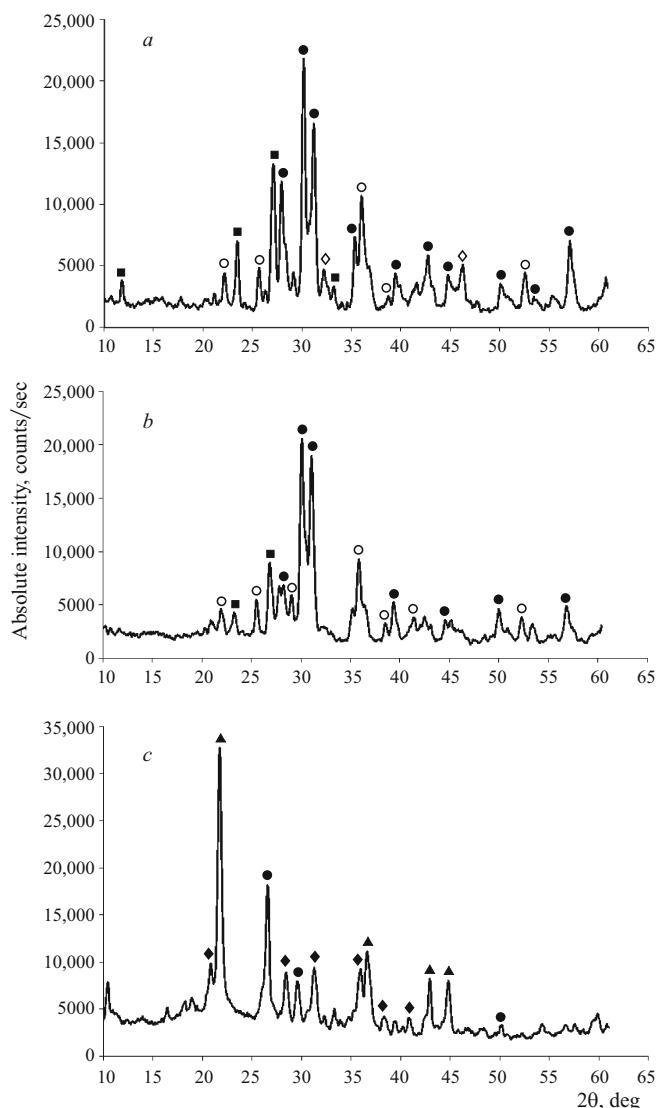
where  $x = 0.1 - 1$  mole; MeO — oxides of the chromophore metal.

Calcination of the pigments was performed at temperatures  $1150 - 1250^\circ\text{C}$  with 1 h soaking at the maximum temperature. Soaking is necessary for complete implantation of the pigments ions into the crystal lattice of the synthesized compounds.

X-ray phase analysis established that the dominant crystalline phase in the pigments obtained from the reaction (7) is diopside ( $d = 0.296, 0.286, 0.218 \text{ nm}$ ) but this could be a solid solution of diopside and magnesium metasilicate, since the peaks are shifted somewhat compared with the reference data and with a sample obtained by the stoichiometric reaction (Fig. 1). Peaks due to magnesium metasilicate ( $d = 0.328, 0.279, 0.211 \text{ nm}$ ), forsterite ( $d = 0.347, 0.249, 0.174 \text{ nm}$ ), and wollastonite residues ( $d = 0.749, 0.272, 0.233 \text{ nm}$ ). A similar picture is obtained for samples obtained by the reaction (8).

Comparing the x-ray diffraction patterns of the samples obtained as a result of stoichiometric and nonstoichiometric reactions (7) and (8) shows that a more perfect structure of diopside is formed in the latter; this is indicated by an increase of the intensity of the diopside peaks (histogram in Fig. 2) and a decrease of the number and intensity of the peaks characteristic for the intermediate products of the reaction (wollastonite, forsterite).

Investigation of the reaction (9) established that a decrease of the amount of magnesium oxide as compared with the stoichiometric amount does not increase the yield of the main reaction product — diopside. The dominant phase in the structure formed is cristobalite ( $d = 0.404, 0.246, 0.169 \text{ nm}$ ); the remaining phases åkermanite ( $d = 0.422, 0.287, 0.251 \text{ nm}$ ) and diopside ( $d = 0.334, 0.303, 0.183 \text{ nm}$ )



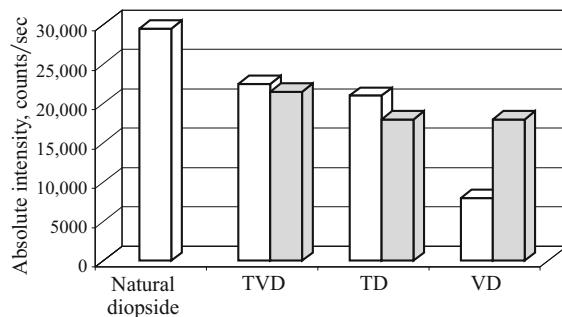
**Fig. 1.** X-ray diffraction peaks of samples obtain by reactions: a) (7), b) (8), c) (9); ●) diopside; ■) wollastonite; ◇) forsterite; ○) magnesium metasilicate; ◆) åkermanite; ▲) cristobalite; calcination temperature  $1200^\circ\text{C}$ .

have approximately the same intensity and number of diffraction peaks (see Fig. 1). However, the dominant diopside structure forms by the stoichiometric reaction. To obtain the best results with respect to diopside yield the content of silicon oxide must be decreased.

Chromophore additions in the amounts 5 – 12 wt.% have no mineralizing effect on the synthesis of the diopside struc-

**TABLE 1.** Chemical Composition of Raw Materials

Raw material	Content, wt.%							Others, %
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{TiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{R}_2\text{O}$	
Algui talc	63.00	0.89	0.14	31.53	Traces	0.06	—	4.70
Micaceous wollastonite	51.70	0.11	46.48	1.23	—	—	0.16	0.32

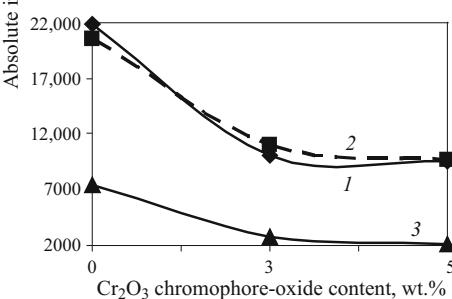
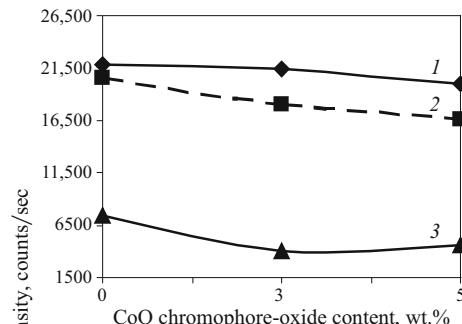


**Fig. 2.** Variation of the absolute intensity of the main diffraction peak characteristic for diopside ( $d = 0.299$  nm); TVD) reaction (7); TD) reaction (8); VD) reaction (9); calcination temperature 1200°C; (white bar) nonstoichiometric reaction; (gray bar) stoichiometric reaction.

ture. As the content of the coloring oxide is increased, the total intensity of the diffraction peaks decreases (Fig. 3). Adding cobalt oxide increases the number of characteristic diopside peaks, which the closeness of the ionic radii of  $\text{Co}^{2+}$  and  $\text{Mg}^{2+}$  (0.082 and 0.078 nm, respectively, according to Goldschmidt) facilitates. The addition of chromium results in disordering of the crystalline structure.

Analysis of the color range of the pigments shows that one and the same chromophores give close color hues in different reactions: nickel — light green, yellow-green; chromium — gray green, grass color; iron — apricot-brown, red-brown, chocolate. Exceptions are cobalt-containing pigments, whose color varied from lilac-rose in the reaction (7) and lilac in the reaction (8) to bright blue in the reaction (9).

It is known [5] that a rose color is characteristic for the ion  $\text{Co}^{2+}$  in octahedral complexes and a blue color is charac-



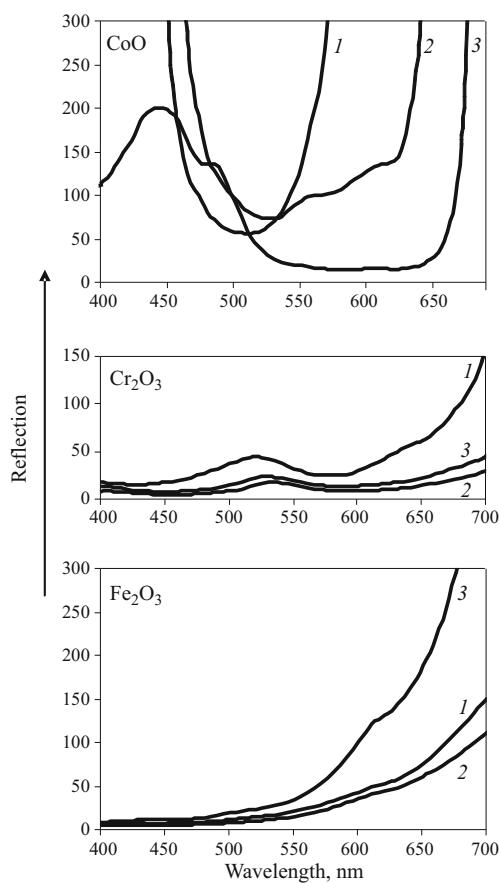
**Fig. 3.** Variation of the intensity of the main diopside diffraction peak ( $d = 0.299$  nm) with the addition of chromophore oxides; calcination temperature 1200°C.

teristic for tetrahedral complexes. The chromophore ions in the diopside structure should preferentially occupy the positions of octahedrally coordinated magnesium ion, although a substitution is possible due to calcium ion, which also are found in octahedral coordination. Since in the reaction (9) it is not a diopside but rather a cristobalite structure that is

**TABLE 2.** Color Characteristics of Pigments Calcined at 1200°C

Pigment	Chromo- phore	Chromo- phore con- tent, wt. %	Color	Chromaticity coordinates			Wavelength $\lambda$ , nm	Hue purity, %
				x	y	z		
Reaction (7)								
TVD-2	SoO	5	Rose	0.39	0.26	0.35	508*	22
TVD-7	NiO	7	Light green	0.37	0.38	0.25	575	32
TVD-11	$\text{Cr}_2\text{O}_3$	13	Very pale green	0.32	0.41	0.27	543	35
TVD-13	$\text{Fe}_2\text{O}_3$	6	Light apricot	0.45	0.36	0.19	595	46
Reaction (8)								
TD-2	SoO	6	Lilac	0.38	0.24	0.38	525*	23
TD-7	NiO	8	Greenish white	0.33	0.38	0.29	550	22
TD-11	$\text{Cr}_2\text{O}_3$	16	Grassy green	0.36	0.46	0.18	561	60
TD-13	$\text{Fe}_2\text{O}_3$	7	Apricot	0.47	0.35	0.18	602	47
Reaction (9)								
VD-1	SoO	4	Azure	0.19	0.18	0.63	475	35
VD-6	NiO	11	Very pale green	0.34	0.41	0.25	556	35
VD-10	$\text{Cr}_2\text{O}_3$	13	Green	0.34	0.43	0.23	555	44
VD-12	$\text{Fe}_2\text{O}_3$	7	Orange-apricot	0.49	0.35	0.16	605	54

\* λ) additional wavelength.



**Fig. 4.** Spectral reflection curves of the pigments (indicated on the curves) obtained by adding chromophore oxides: CoO (a); Cr<sub>2</sub>O<sub>3</sub> (b); Fe<sub>2</sub>O<sub>3</sub> (c): 1 ) reaction (7); 2 ) reaction (8); 3 ) reaction (9).

formed, the formation of a blue color could be due to the tetragonal structural symmetry of  $\beta$ -cristobalite, facilitating the splitting of the  $d$ -sublevel of the Co<sup>2+</sup> ion according to the tetrahedral scheme. In addition, the Mg<sup>+</sup> ions in the  $\text{akermanite}$  structure are located in an environment of four oxygen ions, so that in this case on substitution the Co<sup>2+</sup> ions, falling into tetrahedral coordination, give a blue color.

Figure 4 displays the spectral reflection curves, and Table 2 gives the color characteristics of the pigments. Spectrophotometric analysis of the pigments was performed with an SF-256 spectrophotometer.

Tests on the pigments in the compositions of overglaze paints and tile glazes (Table 3) showed that they are resistance to corrosive effects of fluxes and glazes and are not burned out during calcination. The content (wt.%) of pigment and flux in paints was 20 : 80. Pigments were introduced into glazes in the amounts 5 – 10%.

**TABLE 3.** Color of Overglaze Paints and Glazes

Pigment	Overglaze paint color, $t_{\text{cal}} = 870^\circ\text{C}$	Glaze color, $t_{\text{cal}} = 950^\circ\text{C}$
TVD-2	Azure	Lilac
TD-2	Violet-blue	Lilac
VD-1	Blue	Blue violet
TVD-7	Lemon yellow	Yellowish green
VD-6	Greenish yellow	Sandy
TVD-11	Yellowish green	Olive
TD-11	Red	Green
TD-13	Yellow	Sandy
VD-12	Yellowish brown	Chocolate

It can be concluded on the basis of the present studies that when synthesizing ceramic pigment from natural or chemically pure raw materials, in order to improve the uniformity of the composition of the material obtained and increase the yield of the main product of the reaction some initial component should be used in a nonstoichiometric ratio. The components remaining in the reaction products or the components which on interacting with other reagents can give intermediate compounds should be used in smaller quantities.

## REFERENCES

1. V. M. Pogrebenkov, M. B. Sedel'nikova, and V. I. Vereshchagin, "Obtaining ceramic pigments with diopside structure from talc," *Steklo Keram.*, No. 5, 16 – 18 (1998); V. M. Pogrebenkov, M. B. Sedel'nikova, and V. I. Vereshchagin, "Production of ceramic pigments with diopside structure from talc," *Glass Ceram.*, **55**(5 – 6), 148 – 150 (1998).
2. V. M. Pogrebenkov, M. B. Sedel'nikova, and V. I. Vereshchagin, "Ceramic pigments with diopside and anortite structure based on wollastonite," *Steklo Keram.*, No. 2, 18 – 20 (1999); V. M. Pogrebenkov, M. B. Sedel'nikova, and V. I. Vereshchagin, "Ceramic pigments with diopside and anortite structure based on wollastonite," *Glass Ceram.*, **56**(1 – 2), 55 – 57 (1999).
3. A. V. Belyakov, "Effect of the differences in the diffusion coefficients of cations on the deviation from stoichiometry in complex oxides," *Steklo Keram.*, No. 10, 18 – 20 (1997); A. V. Belyakov, "The effect of a difference in the diffusivity of cations on the deviation from stoichiometry in complex oxides," *Glass Ceram.*, **54**(9 – 10), 317 – 319 (1997).
4. P. P. Budnikov and P. P. Ginstling, *Reactions in Mixtures of Solid Substances* [in Russian], Stroiizdat, Moscow (1971), 3rd edition, corrected and supplemented.
5. G. N. Maslennikova and I. V. Pishch, *Ceramic Pigments* [in Russian], RIF "Stroimaterialy" JSC, Moscow (2009).